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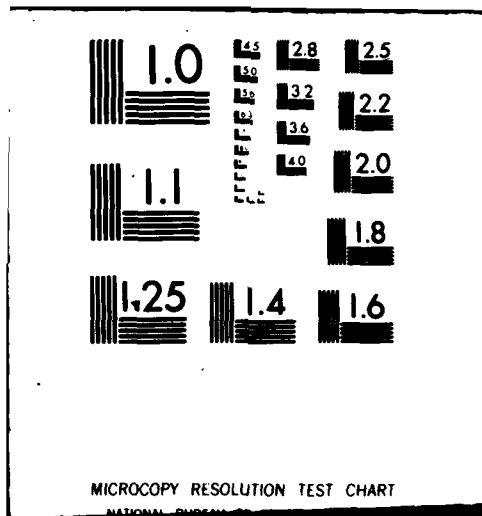
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Report No. FAA-RD-79-62

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**RESTORING ESSENTIAL FLOW AND  
IGNITION PROPERTIES TO ANTIMISTING KEROSENE  
(AMK) FOR TURBINE AIRCRAFT OPERATIONS**

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**FEBRUARY 1979**

**FINAL REPORT**

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16. Abstract Flow properties of antimisting kerosine (0.3% FM-9 in Jet A), such as filtration resistance and apparent viscosity, are greatly improved by increasing the temperature to 140°C or by the addition of a fuel-soluble surfactant. This is achieved by preventing flow-induced hydrogen bonding that results in the buildup of a gel-like structure. Flow in porous media appears to be a promising method of producing polymer degradation; however, energy levels higher than 7 kW/l will be required to reduce both filtration and ignition properties of antimisting kerosine (AMK) to that of Jet A.  A small-scale test has been used to measure the resistance of a fuel to form a mist that will support flame propagation. Preliminary results indicate that this measurement is in good agreement with other large-scale fire safety tests.  The ignition resistance of AMK has been found to depend on fuel properties such as aromatic content and the presence of polar additives. The most controversial result of these experiments is that in addition to improving filterability, surfactants increase the ignition resistance of AMK. While the rheological mechanism for this has not been established, several factors suggest that it is associated with improved solubility of the polymer.		13. Type of Report and Period Covered Final Report. 26 Apr 1978-31 Jan 1979	
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## PREFACE

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Mr. M.K. Greenberg of SwRI performed the rheological and mechanical degradation studies, and Mr. J.L. Jungman of SwRI performed the mist ignition measurements.



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# LIST OF SYMBOLS

- A - Cross-sectional area
- AMK - Antimisting kerosine
- C - Polymer concentration
- $d_p$  - Bead diameter in packed tube
- K - Permeability of packed tube
- L - Length
- LIR - Lower ignition resistance
- Q - Flow rate of AMK
- $Q_o$  - Flow rate of solvent (Jet A)
- R - Radius of capillary tube
- R(T) - filtration ratio ( $Q_o/Q$ ) of Jet A relative to AMK
- UIR - Upper ignition resistance
- $\gamma$  - Maximum shear rate in capillary tube
- $\Delta P$  - Pressure drop for AMK
- $\Delta P_o$  - Pressure drop for solvent (Jet A)
- $\eta$  - Viscosity of AMK
- $\eta_o$  - Viscosity of solvent (Jet A)
- $\eta_r$  - Viscosity ratio ( $\eta/\eta_o$ )
- $\frac{\eta_{r-1}}{c}$  - Reduced viscosity
- [ $\eta$ ] - Intrinsic viscosity
- $\tau$  - Maximum shear stress in capillary tube
- $\phi$  - Porosity of packed tube



## I. INTRODUCTION

Catastrophic effects of post-crash aircraft fires continue to be costly in terms of passenger lives, resources consumed, and deterrence to air travel. The current trend to larger aircraft carrying more passengers emphasizes the need to develop an operational aviation fuel that will improve fire safety under survivable ground crash conditions.

In a typical survivable crash, tanks and lines rupture on impact and discharge fuel into the air as the momentum thrusts the aircraft forward along the ground at high speed. The fuel contacting the high-velocity airstream is atomized into finely divided droplets to form a highly flammable (usually explosive) mist. Following this, the resulting mist fireball acts as a primary ignition source for the remainder of the fuel that spills to the ground as the damaged aircraft comes to rest.

Antimisting kerosine (AMK) fuel contains a high molecular weight polymer that resists the formation of small droplets and has been shown to improve fire safety in simulated tests of ground crash conditions; however, poor fuel filtration and atomization characteristics preclude its use in aircraft turbine engines and fuel systems until acceptable means for restoring the essential fuel properties can be developed.

## II. OBJECTIVES

The primary objectives of this program are the development of a suitable method of restoring the essential flow and ignition properties of AMK so that it will perform satisfactorily in aircraft turbine engines and fuel-delivery systems, as well as the development of measurement techniques that will characterize the fire-safety and rheological properties of AMK.

## III. APPROACH

Filtration studies were performed with nominal 10-micrometer filter paper and a fixed pressure gradient of 0.5 psi; however, additional rheological experiments were conducted with packed tubes that relate to

filtration, in which effects of pressure gradient and pore size were also investigated. Similar experiments were performed with capillary tubes of different length and diameter to characterize the laminar shear flow properties of AMK. Polymer degradation was produced by flow in a tube packed with uniform glass beads, while the resistance of AMK to form an ignitable mist was measured with a spinning disc atomizer.

#### IV. EXPERIMENTAL RESULTS

##### A. Flow Characteristics

##### 1. Laminar Flow in Capillary Tubes

The shear characteristics of 0.3% FM-9\* antimisting polymer in Avtur\*\* have been reported earlier.<sup>(1)\*\*\*</sup> Below a critical shear stress that is generally between 25 and 50 dyn/cm<sup>2</sup>, the viscosity is approximately constant and is 1.5 to 1.6 times higher than the base fuel. When the stress is increased above the critical value, there is an upturn in the flow curve, after which the apparent viscosity increases with both stress and time in a complex manner. Upon reduction of the stress below the critical value, a hysteresis loop is usually observed. Experiments with 0.3% FM-9 in Jet A have confirmed these earlier findings.

With the exceptions of high molecular weight ( $5 \times 10^6$ ) poly (methyl methacrylate) in theta solvents<sup>(2-6)</sup> and copolymers of methyl methacrylate and methacrylic acid<sup>(7)</sup>, this type of rheological behavior (anti or negative thixotrophy) is very rare for dilute polymer solutions made with low viscosity solvents. The behavior of the methacrylate and methacrylic acid copolymer has been shown to be a result of flow-induced hydrogen bonding followed by the build-up of a supermolecular or gel-

\* Imperial Chemical Industries Limited.

\*\* British Jet Fuel RD 2494.

\*\*\* Superscript numbers in parentheses refer to the list of references at the end of this report.

like polymer structure. Furthermore, it has been shown that strong hydrogen-bonding agents such as dimethylformamide (DMF) prevent flow-induced gelation. While DMF was not found to be soluble in Jet A, other fuel-soluble amides (surfactants) were used that had a remarkable effect on the rheological properties of AMK. In particular, after 0.5 wt% SO-A\* is added to 0.3% FM-9 in Jet A, the fuel no longer gels when it is vigorously shaken.

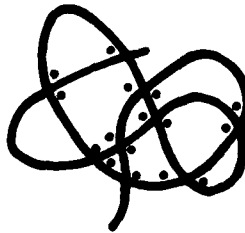
A possible explanation of flow-induced gelation of FM-9 and the apparent removal of this phenomenon by SO-A is presented in Figure 1. Since gel formation involves hydrogen bonding, the FM-9 polymer must necessarily contain polar groups that are oleophobic. Consequently, it is quite possible that the FM-9 behaves much like a micellar system in which these polar sites are hidden from the fuel by the polymer backbone (Figure 1a.) In a nonflowing solution, this would bring the polar species relatively close together and promote the formation of hydrogen bonding. The net results of this intramolecular hydrogen bonding would be a tight polymer coil and effectively low-intrinsic viscosity. In a flowing system, the stress acting on the polymer increases with increasing shear rate and may result in significant deformation of the polymer coil and exposure of polar groups. As polymer molecules along adjacent streamlines are brought into contact by the velocity gradient, the exposed polar groups enter into intermolecular hydrogen bonding with the buildup of a super molecular structure that leads to gel formation.

Hydrogen bonding agents such as amide-type surfactants probably adsorb on these polar sites in such a way that the oleophilic portions of the surfactant shield them from the fuel. This effectively increases the solubility of the polymer, expands the polymer coil, and increases the intrinsic viscosity (Figure 1b). Since the relaxation time of a dilute polymer solution is related to molecular size and flexibility, the net effect should be increased viscoelasticity. In addition to increasing viscoelasticity, the protective shielding of the polar groups by the surfactants would also be expected to resist flow-induced intermolecular hydrogen bonding and gel formation.

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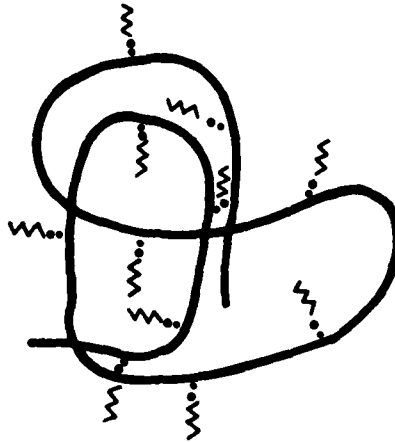
\* Scher Chemicals Inc., Clifton NJ.

a) **FM-9 WITHOUT SURFACTANT**  
**INTRAMOLECULAR HYDROGEN BONDING**  
**REDUCES MOLECULAR SIZE**



• — POLAR SITES

b) **FM-9 WITH SURFACTANT**  
**HYDROGEN BONDING BETWEEN SURFACTANT**  
**AND POLAR SITES ON FM-9 INCREASES**  
**MOLECULAR SIZE**



~ — SURFACTANT MOLECULE

FIGURE 1. EFFECT OF SURFACTANT ON FM-9 ANTIFISTING POLYMER

The results of experiments that demonstrate the effect of SO-A on the flow resistance or apparent viscosity of AMK in capillary tubes are presented in Figures 2 through 4. In these experiments, measurements of the flow rate are made at several different pressures ( $\Delta P$ ). The results in Figure 2 show that data for Jet A produce a straight line that passes through the origin. The viscosity ( $\eta_0$ ) of Jet A can be calculated from the ratio of the wall maximum shear stress at the tube wall ( $\tau = R \Delta P / 2L$ , where  $R$  is the tube radius,  $\Delta P$  is the pressure drop, and  $L$  is the tube length) to the maximum shear rate ( $\dot{\gamma} = 4Q / \pi R^3$ , where  $Q$  is the flow rate). Actually, the quantity  $4Q / \pi R^3$  is the shear rate only if the fluid is Newtonian; however, this second order correction has been neglected for the present.

Below a critical pressure gradient of between 4 and 5 psi, the data for AMK with 0.5% SO-A are also linear. The ratio of the slope of the linear portion of this curve to the slope of the Jet A curve ( $\Delta P / \Delta P_0$ ) is equal to the viscosity ratio ( $\eta_r = \eta / \eta_0$ ) of AMK relative to Jet A. Based on the data in Figure 2,  $\eta_r$  is equal to 1.8 for AMK with 0.5% SO-A; earlier measurements resulted in  $\eta_r$  being equal to 1.5 for AMK without SO-A. The intrinsic viscosity,  $[\eta] \equiv \lim_{C \rightarrow 0} (\eta_r - 1) / C$ , is calculated from the reduced viscosity  $(\eta_r - 1) / C$ , where  $C$  is the concentration of FM-9. Consequently, the observed change in the viscosity ratio due to SO-A indicates a very significant increase in the intrinsic viscosity, e.g.,  $(1.8 - 1) / (1.5 - 1) = 1.6$  or about a 60% increase. Since changes in the intrinsic viscosity should be directly related to changes in the relaxation time of the polymer solution<sup>(8)</sup>, these results indicate that SO-A should increase the viscoelasticity of AMK made with the FM-9 polymer.

Above 4 psi, a shear-thickening effect is noted by the increase in slope of the flow curve. Consecutive measurements of the flow rate at a constant pressure showed no evidence of time dependency or hysteresis even when the pressure was reduced below 4 psi. However, the time scale of these pressure changes was of the order of a minute, and if FM-9/SO-A is highly viscoelastic, it is quite possible that time effects would be

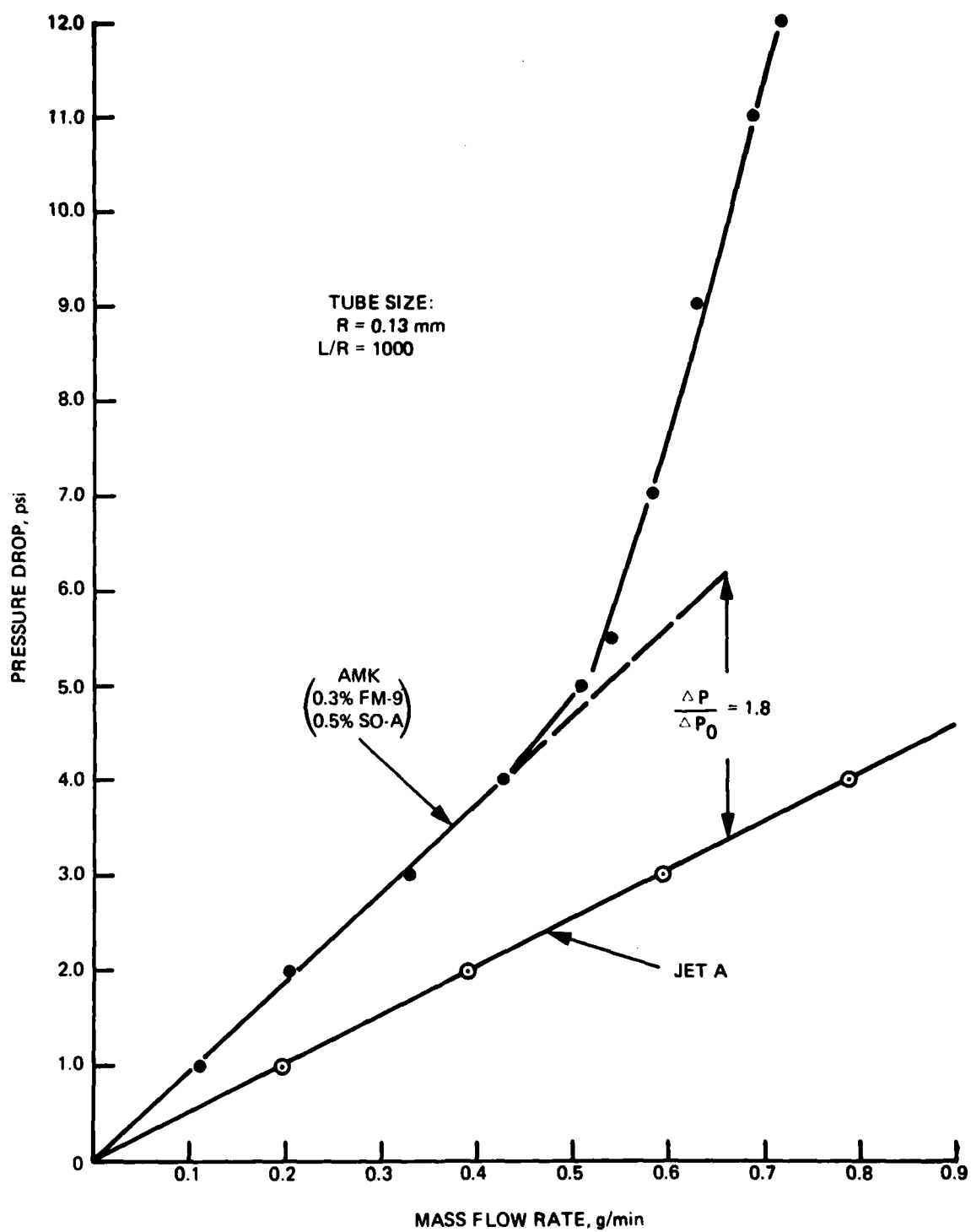


FIGURE 2. SHEAR THICKENING OF FM-9/SO-A  
IN CAPILLARY TUBE FLOW

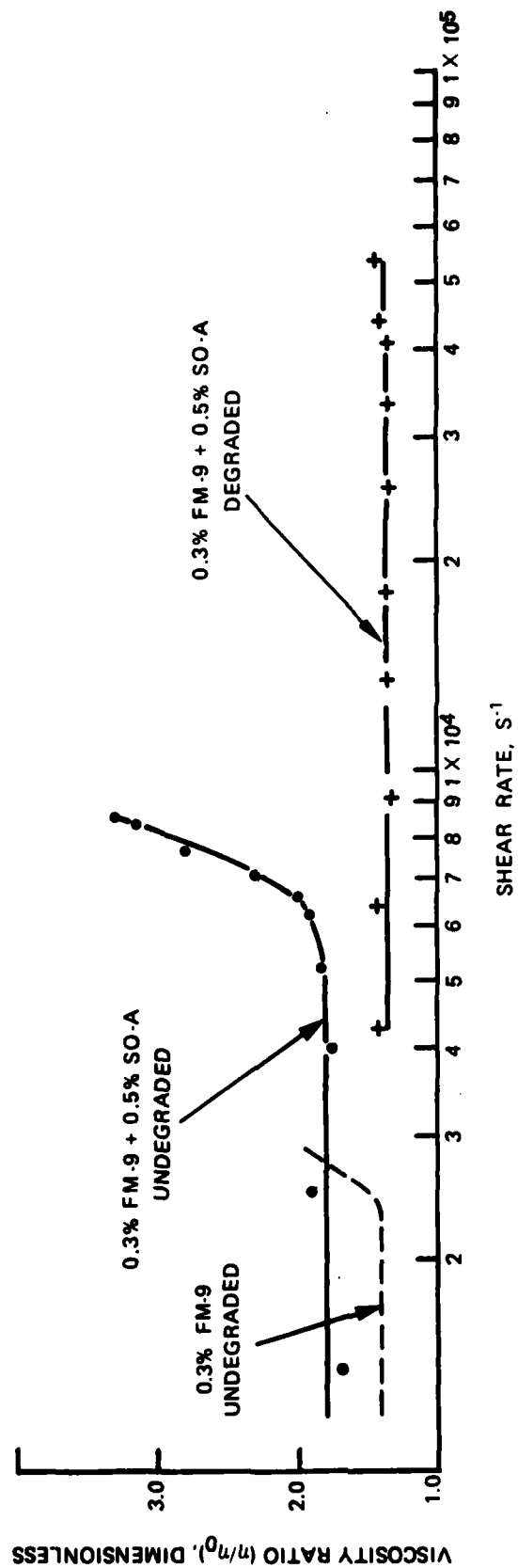


FIGURE 3. EFFECT OF MECHANICAL DEGRADATION ON SHEAR THICKENING OF FM-9/SO-A IN CAPILLARY FLOW

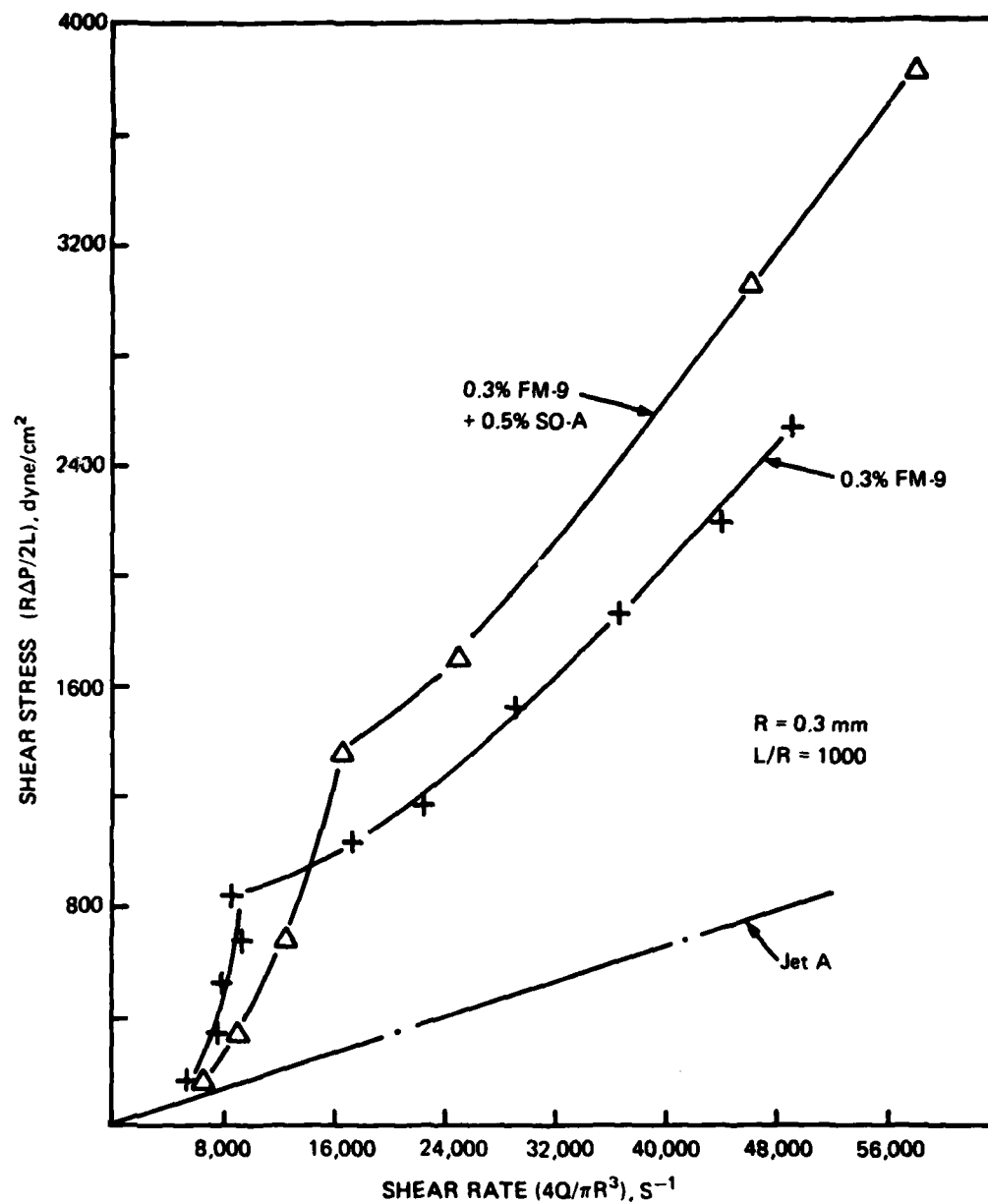


FIGURE 4. EFFECT OF SURFACTANT ON SHEAR THICKENING OF FM-9 IN JET A



observed if the experimental time scale was of the order of a few seconds. These suspected effects could be important in fuel control systems where a rapid change in fuel flow may occur; consequently, experiments are necessary to investigate the viscoelastic time effects of AMK at flow conditions above the critical.

The effect of mechanical degradation on the shear characteristics of AMK with 0.5% SO-A in capillary tubes are shown in Figure 3. In this case, degradation was produced by one pass through a packed tube ( $d_p = 810 \mu m$ ,  $A = 0.15 \text{ cm}^2$  and  $L = 3.4 \text{ cm}$ ) with a pressure drop of 1000 psi (7 kW/l). The critical shear rate of the degraded sample was too high to determine and was certainly in excess of  $50,000 \text{ s}^{-1}$ . This value is at least an order of magnitude higher than undegraded AMK that contains 0.5% SO-A. While it was hoped that the critical shear stress or shear rate could be used to characterize polymer degradation, the fact that SO-A increases the critical shear rate (Figure 3) without degrading the polymer shows that a higher critical shear rate is not sufficient to ensure polymer degradation.

The results of preliminary experiments at high shear stresses indicate that there is a second critical stress above which AMK no longer shear thickens (Figure 4). Thus, while the onset of shear thickening occurs at a lower shear stress without the surfactant ( $50 \text{ dyn/cm}^2$  compared to  $150 \text{ dyn/cm}^2$ ), the shear-thickening process terminates sooner ( $800 \text{ dyn/cm}^2$  compared to  $1400 \text{ dyn/cm}^2$ ). It is possible that this second critical stress may be a useful criterion; however, this possibility must be verified by additional experiments.

## 2. Filtration Resistance

The ratio of the filtration rate of Jet A at  $27^\circ\text{C}$  to AMK at any temperature is defined as  $R(T)$  and is a measure of the relative flow resistance through the filter under a specific set of experimental conditions. For these experiments, the filter size (nominal 10-micrometer paper), diameter (47 mm), and pressure gradient (0.5 psi) were held constant. The results in Figure 5 show that increasing the temperature

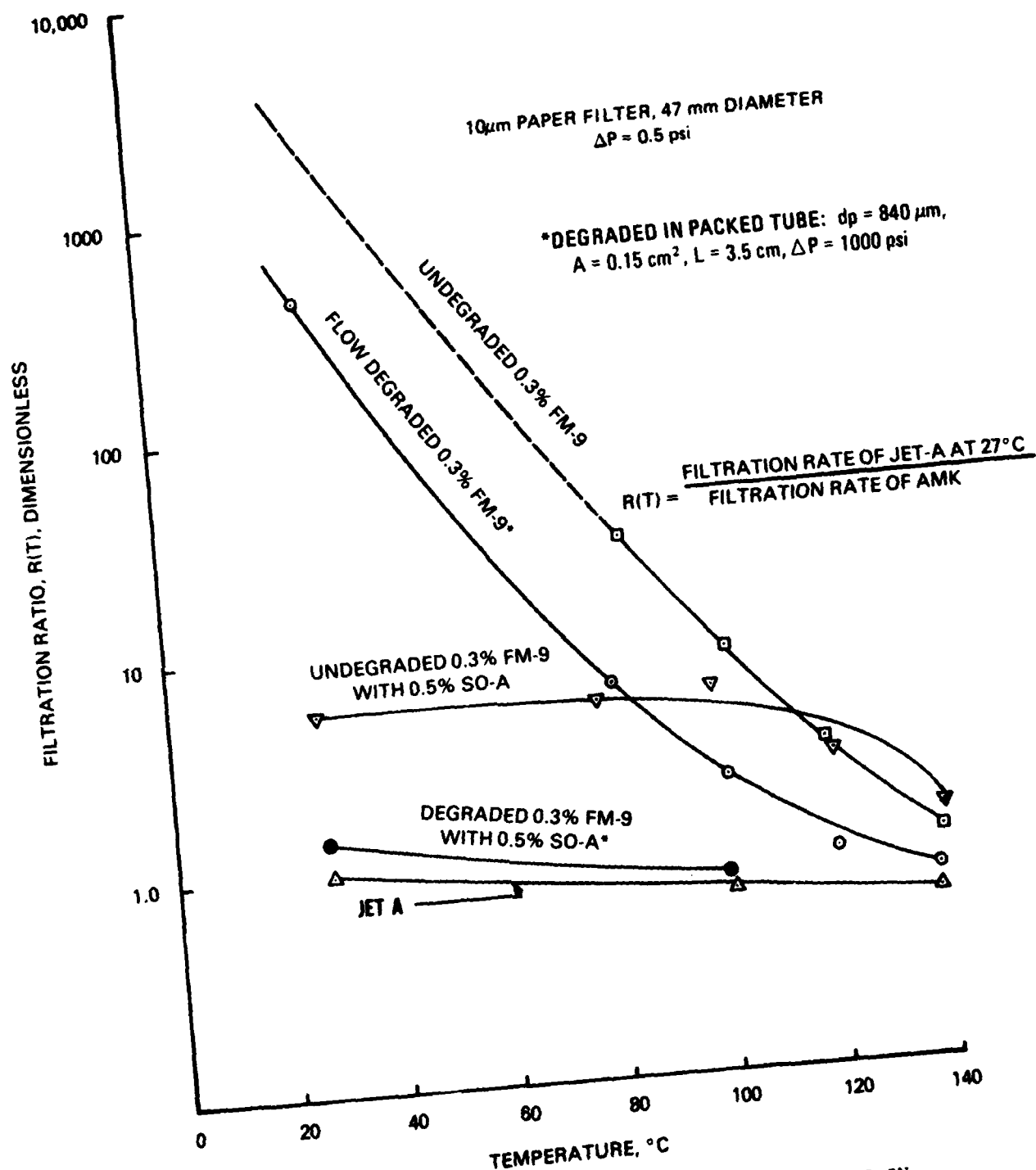


FIGURE 5. EFFECT OF TEMPERATURE, DEGRADATION AND SURFACTANT ON FILTRATION RATIO,  $R(T)$  OF FM-9 IN JET A

rapidly reduces the filtration ratio of undegraded AMK (0.3% FM-9 in Jet A) from several thousand at 27°C to close to 1 at 140°C. This decrease in the ratio is most probably associated with reduced hydrogen bonding at elevated temperatures. Flow degradation of AMK in a packed tube ( $d_p = 840 \mu\text{m}$ ,  $A = 0.15 \text{ cm}^2$ ,  $L = 3.5 \text{ cm}$ , and  $\Delta P = 1000 \text{ psi}$ ) reduced  $R(27^\circ\text{C})$  from several thousand to several hundred. However, much higher pressure gradients would be required to obtain a room temperature filtration ratio that is close to Jet A.

Filtration experiments in which 0.5% SO-A was added to AMK showed that the surfactant reduced  $R(27^\circ\text{C})$  from several thousand to 5. The fact that  $R(T)$  remained essentially constant over the range of 27° to 120°C indicates that the surfactant is effectively preventing polymer-polymer hydrogen bonding. Flow degradation in a packed tube reduced  $R(27^\circ\text{C})$  from 5 to 1.4 with a specific energy expenditure ( $\Delta P$ ) of 7 kWs/l. This low resistance would normally be expected to indicate a high degree of polymer degradation. However, experiments in packed tubes that relate to filtration indicate that the filtration resistance is a function of filter pore size and pressure gradient. Consequently, partially degraded AMK, which has a filtration resistance similar to Jet A under certain conditions, may suddenly exhibit a very high resistance if either the pressure gradient is increased or the pore size decreased.

### 3. Flow Characteristics in Porous Media

Flow in porous media has been found to be a useful tool for characterizing viscoelastic antimisting polymers.<sup>(1)</sup> Typically, the shear viscosity of dilute solutions of high molecular polymers decreases with shear rate; however, in porous media, such as packed tubes, there is an upturn in the flow curve that is believed to be associated with a sudden increase in the elongational or tensile viscosity.<sup>(9)</sup> It is important to reiterate that, with the exceptions of poly (methylmethacrylates) and copolymers of methyl methacrylate and methacrylic acid, most polymers do not exhibit this increase in resistance in capillary tube flow even at very high shear rates.

Experiments were performed with tubes ( $A=0.28 \text{ cm}^2$ ) packed with uniform glass beads. The porosity ( $\phi$ ) was calculated from the weight of glass beads (density = 2.42 g/ml) in a given volume, and was essentially the same value (0.36-0.38) for different size beads. Flow data for Jet A and AMK (0.3% FM-9 in Jet A) with 0.5% SO-A are presented in Figure 5. The flow curve for Jet A is a straight line that passes through the origin. The permeability ( $K$ ) of the porous media was calculated from the slope of this line ( $\Delta P/Q$ ), the viscosity of Jet A ( $\eta_o$ ), and the dimensions of the tube ( $L$ ,  $A$ ) by using the Darcy Equation:

$$K = \eta_o L / A(\Delta P/Q) \quad (1)$$

The value  $146 \times 10^{-8} \text{ cm}^2$  (146 Darcies) is in good agreement with the permeability of  $150 \times 10^{-8} \text{ cm}^2$  calculated for a bed of uniform spherical particles ( $d_p = 420 \text{ }\mu\text{m}$ ,  $\phi = 0.37$ ) by the Kozeny Equation:

$$K = d_p^2 \phi^3 / 150(1-\phi)^2 \quad (2)$$

This excellent agreement was also observed for the smaller beads ( $210 \text{ }\mu\text{m}$ ) and is a good check on the uniformity of the porous media. Typical results for AMK with 0.5% SO-A are also presented in Figure 6. At pressure gradients below 0.4 psi, the curve is linear and the ratio of the slopes of this line relative to Jet A ( $\Delta P/\Delta P_o = 1.7$ ) is very close to viscosity ratio ( $\eta_r = 1.7$ ) measured with a conventional viscometer. In this region, the relative flow resistance ( $\Delta P/\Delta P_o$ ) at a given flow rate is the same as the filtration ratio ( $Q_o/Q$ ) at a given pressure drop. As with the capillary tube experiments, there is an upturn in the flow curve that is indicative of increased flow resistance. Furthermore, the absence of gel formation is evident from the fact that there is no hysteresis when the pressure gradient is reduced. It is important to point out that this is very different from results for AMK without surfactant, in which case no measurable flow can be detected, and there is a permanent loss in permeability due to gel formation.

While the deformation rate in porous media is a combination of shear and elongation, in porous media consisting of uniform spherical particles,

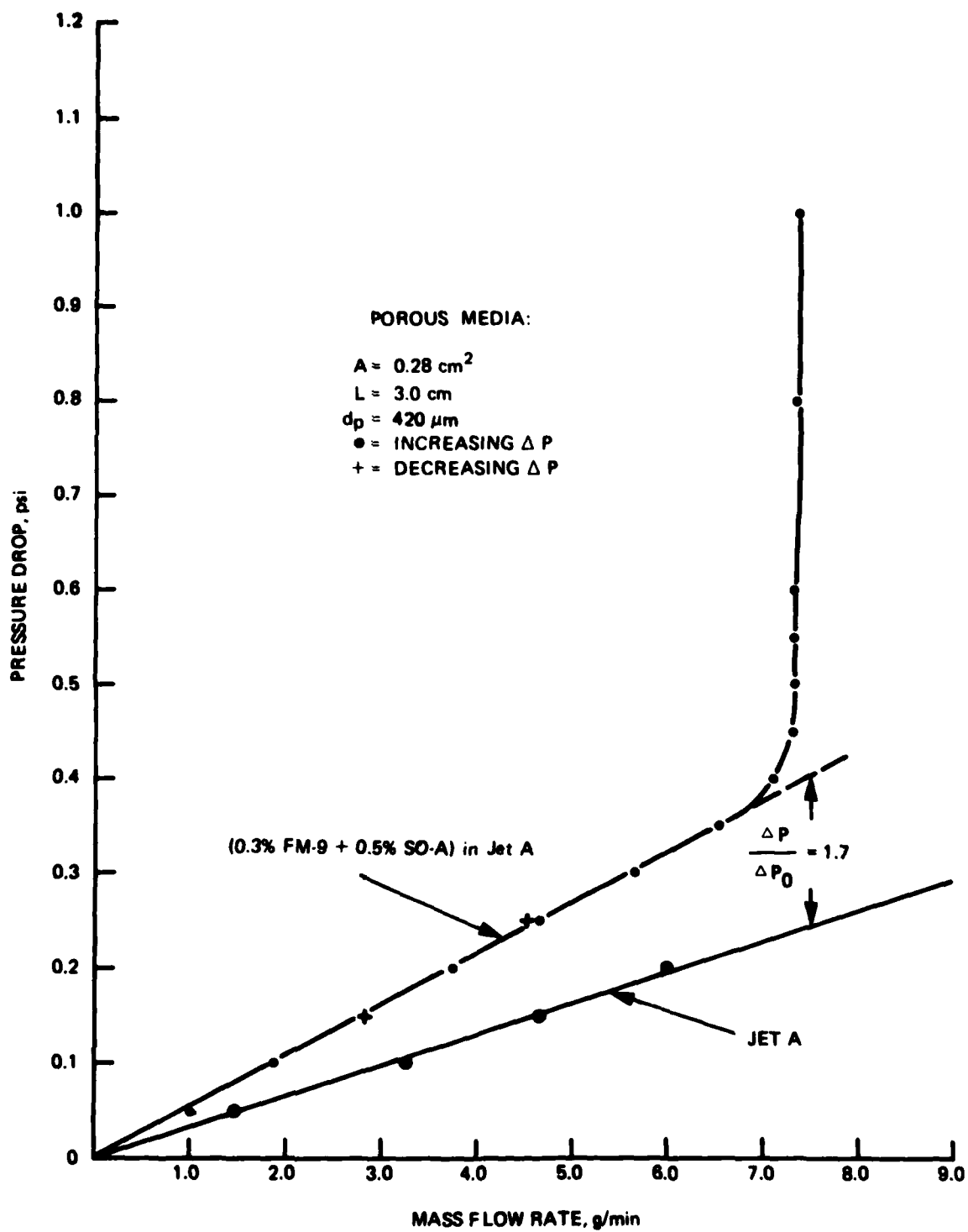


FIGURE 6. EFFECT OF PRESSURE GRADIENT ON FLOW RESISTANCE OF FM-9/SO-A IN POROUS MEDIA

the deformation rate is primarily elongational and of the order of  $Q/Ad_p \phi$ .<sup>(9)</sup>

Since the deformation rate in a packed tube is inversely proportional to the bead size, the onset of high resistance should occur at proportionately lower flow rates with smaller beads. When experiments were conducted with smaller beads (210 compared to 420-micrometers), the data in Figure 7 show that the critical flow rate was reduced from 7 to 3 g/min. This effect of bead diameter on the critical flow rate for viscoelastic resistance in packed tubes is in good agreement with dilute solutions of viscoelastic polymers such as polyisobutylene<sup>(10)</sup>, and is very important in that it may help to design filters that will be able to avoid high flow resistance. In addition to establishing the importance of bead size, the data in Figure 7 are an example of an unusual flow anomaly. As with the larger beads, there is a Newtonian region where the flow resistance is essentially identical with the shear viscosity. As the pressure gradient is increased, there is a sudden upturn followed by a decrease in the flow rate. Normally, such behavior could be explained by a loss in permeability; however, upon reducing the pressure gradient the flow rate at first increased and then decreased in a reversible manner (Figure 7). These experiments were repeated with the larger diameter beads, and a similar reduction in flow rate was observed; however, a higher pressure gradient was required than was used in the first experiment. Since this phenomenon has only been observed for AMK with surfactant in packed tubes, there is good reason to suspect that it is a viscoelastic effect that requires an elongational flow field.

The results in Figure 8 summarize the effects of mechanical degradation with different types of porous media on the flow properties of AMK in a packed tube. The critical pressure gradient for AMK with surfactant is shifted to higher values by mechanical degradation. However, once the critical pressure gradient is exceeded, very high resistances can occur. This sudden change in resistance is particularly important in view of the fact that each of the degraded samples had a filtration ratio close to 1 at the conditions of the filtration experiments (10-micrometer paper, 0.5 psi). Consequently, changes in experimental conditions, such

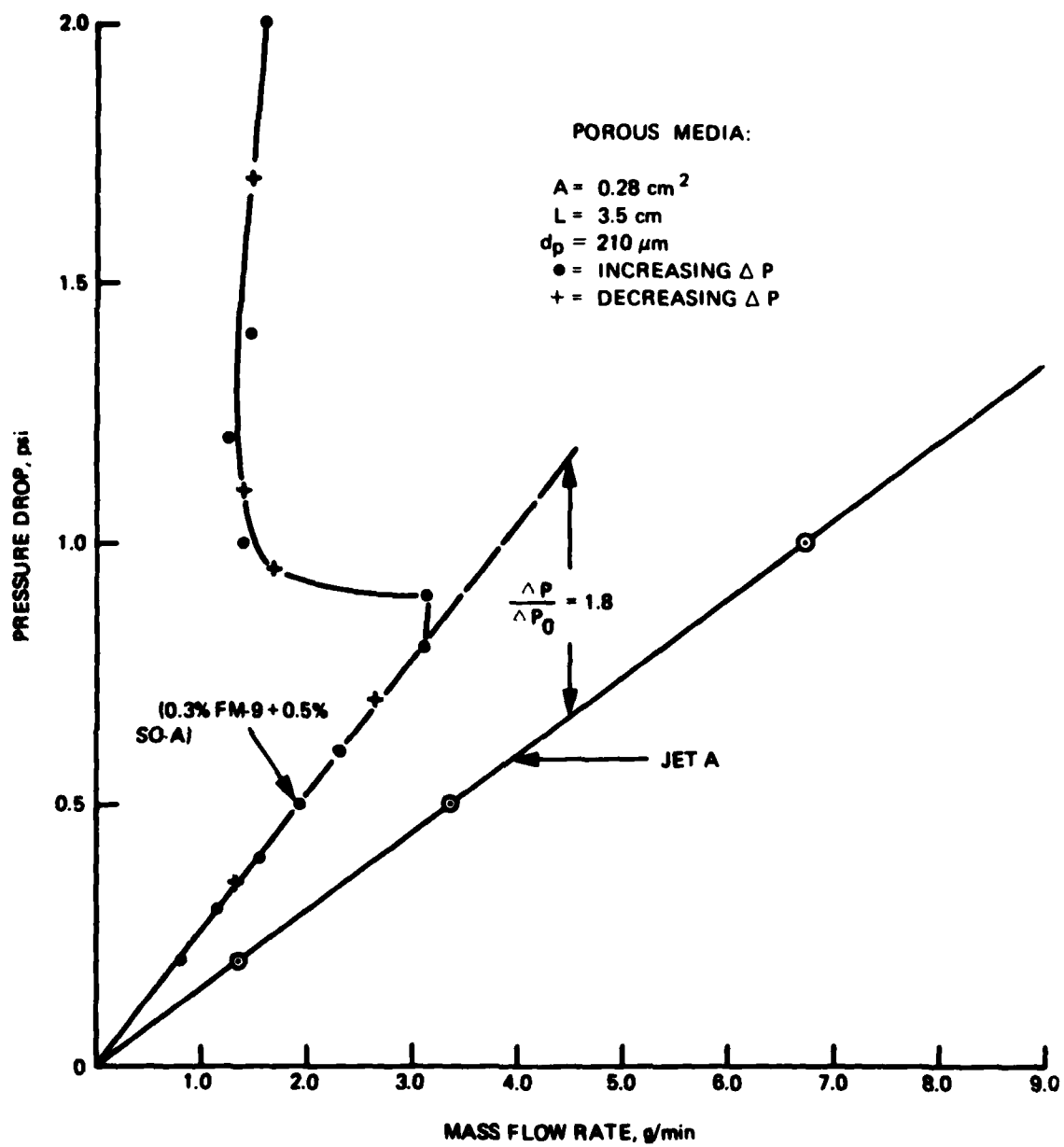


FIGURE 7. FLOW ANOMALY FOR FM-9/SO-A IN POROUS MEDIA

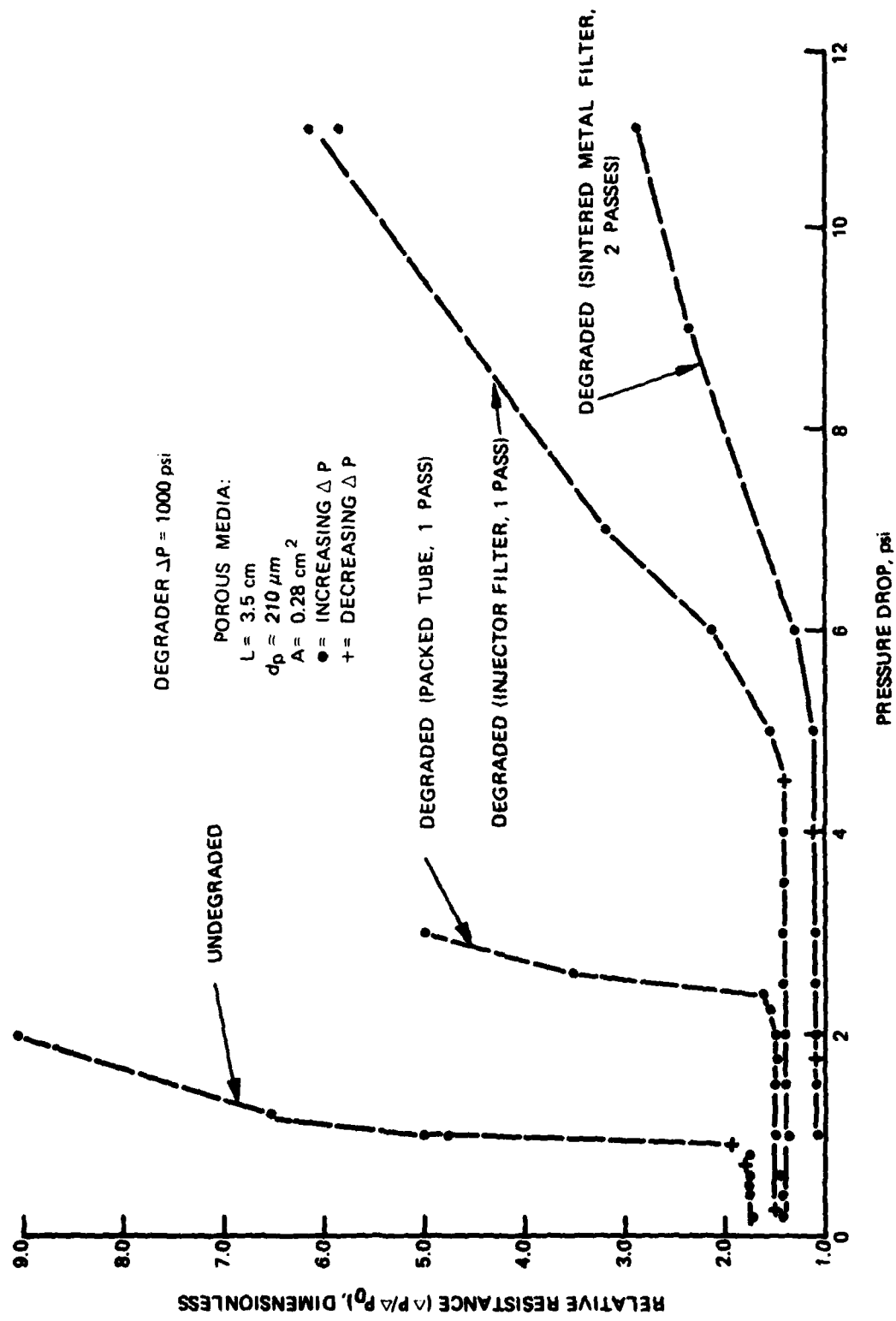


FIGURE 8. EFFECT OF DEGRADATION ON RELATIVE FLOW RESISTANCE OF (0.3% FM-9 + 0.5% SO-A) IN JET A



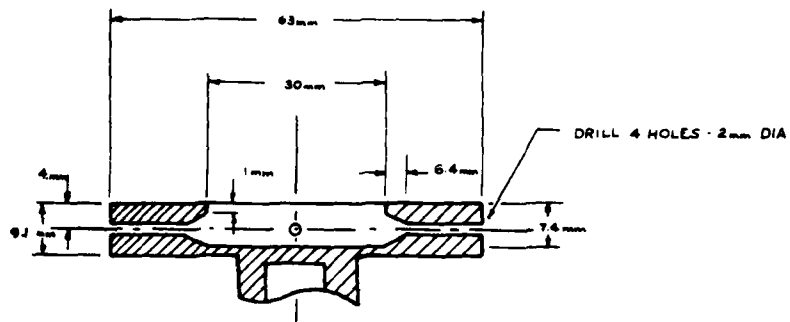
as decreasing the effective pore size or increasing the pressure gradient, could have resulted in very high filtration ratios.

### B. Mist Ignition

A spinning disc atomizer has been used to measure the effects of several variables (polymer and surfactant concentration, fuel properties, temperature and mechanical degradation) on the resistance of AMK to form an ignitable fuel mist. Figure 9a is a sketch of the disc in which four radially spaced 2-mm ID holes are provided as fuel passageways. Because of the relatively large size of these holes, the shear rate ( $4Q/\pi R^3$ ) of AMK relative to the disc can be kept below  $5000 \text{ s}^{-1}$ ; consequently, it is unlikely that any polymer degradation will occur before the AMK contacts the air. In Figure 9b, fuel is shown flowing into the central cavity in the disc head while the oxy-acetylene ignition source (not shown) is approximately 10 cm from the edge of the disc. The mist-ignition resistance is measured by increasing the disc speed until the onset of flame propagation is first observed. The two disc speeds that bracket this condition are recorded as the lower ignition resistance (LIR). At speeds above the LIR, flame propagation increases until the disc is engulfed in fire (Figure 9c). The speeds that bracket this condition are recorded as the upper ignition resistance (UIR).

The results in Figure 10 compare the effects of fuel flow rate on the mist ignition resistance of Avtur (flash point =  $38^\circ\text{C}$ ) and an aged sample of 0.3% FM-9 in Avtur\*. Over the range of 0.5-1.5 l/m, fuel flow rate had only a slight effect on the ignition resistance of either Avtur or AMK. However, at flow rates below 200 ml/min, the ignition resistances of even Avtur become very high.<sup>(11)</sup> It is most likely that this high ignition resistance at low flow rates is due to the spacing between adjacent drops being too large to support flame propagation. In order to avoid this problem, ignition resistance measurements are made at a fuel flow rate of 1 l/min.

\* This sample was blended at RAE on May 19, 1978 and mist ignition measurements were made at SwRI on September 27, 1978 or approximately 4.5 months later.



(A) CROSS SECTION OF DISC



(B) FUEL FLOWS INTO CAVITY



(C) VELOCITY OF DISC PRODUCES  
IGNITABLE FUEL MIST

FIGURE 9. MIST IGNITION APPARATUS

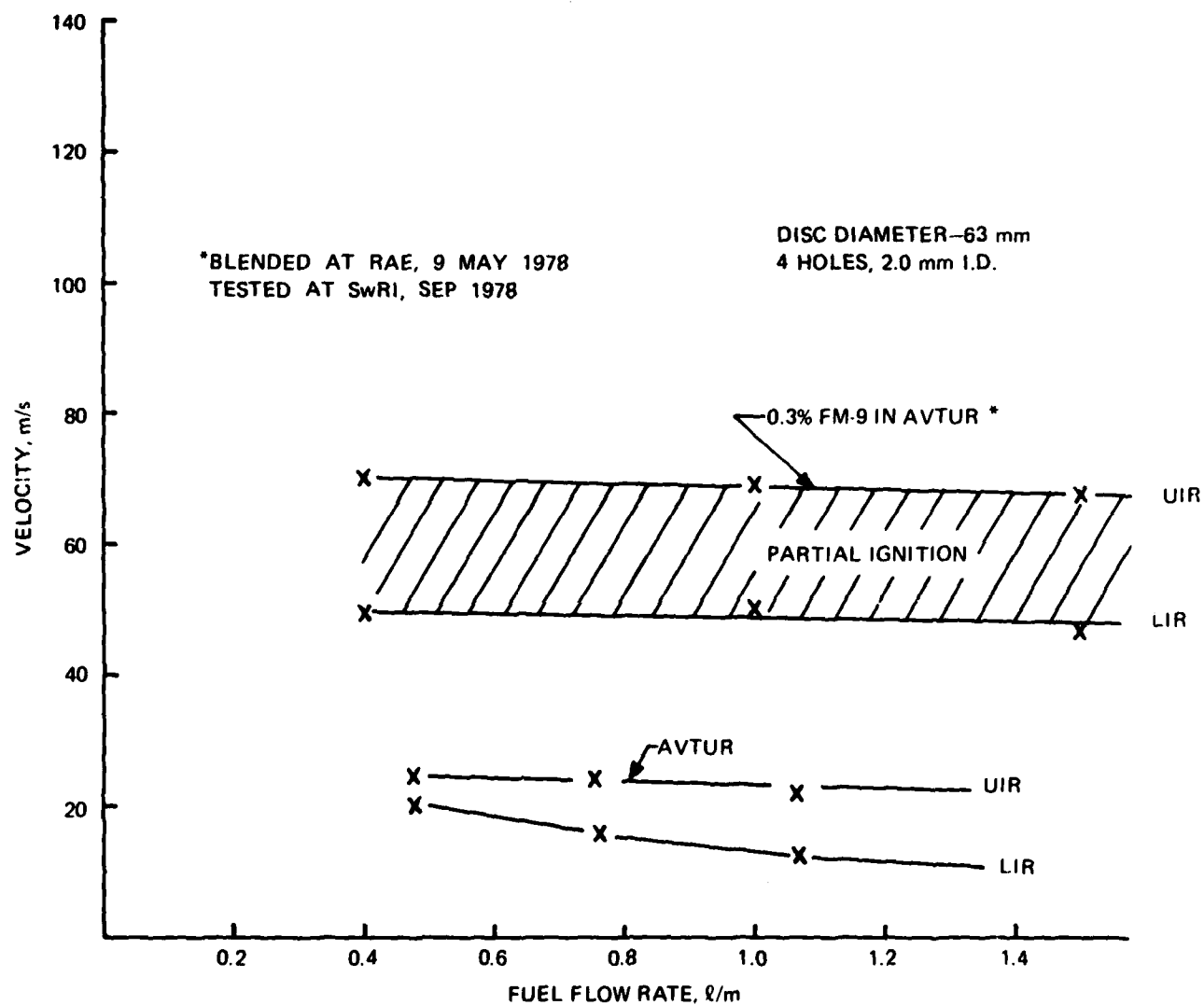


FIGURE 10. EFFECT OF FM-9 ON MIST IGNITION RESISTANCE

The improved fire safety of AMK over Avtur is shown by the higher ignition resistance (50-70 m/s compared to 12-24 m/s). It is important to note that while the ignition resistance of the aged AMK is significantly higher than Avtur, it would be expected to fail or at best be a marginal pass in the standard (66 m/s) rocket test and fail the three rocket (88 m/s) test. This is in agreement with reports that 0.3% FM-9 in Avtur often fails the standard two rocket test after it has been stored for several months.<sup>(12)</sup>

In Figure 11, mist-ignition measurements are compared with the air speeds required for failure of AMK in fuel spillage tests.<sup>(13)</sup> The excellent agreement between the small-scale and the relatively large-scale test (50 to 150 gallons of fuel) over the range of 0.3-0.5% FM-9 in Jet A suggests that the measurement of ignition resistance may be a simple way of characterizing fire-safety effectiveness. However, these preliminary results need to be verified by additional large-scale tests.

Early in this program, it was noticed that the dissolution of FM-9 powder in Jet A was more difficult than in Avtur. Furthermore, orifice flow measurements\*, which are used as a means of quality control, gave a value of 6.7 for 0.3% FM-9 in Jet A. Typically AMK is considered to be substandard unless the orifice flow value is less than 4. An aromatic analysis (ASTM D 1319) showed that the fuel contained only 8 vol% aromatics as opposed to 16- to 18-percent for typical Jet A. When the aromatic content of the fuel was increased to 18 percent with a high (99%) aromatic cut (BP-156°-178°C), the orifice flow value decreased to 3.9. More recently, substandard AMK, as indicated by an orifice flow of 5.7, has been reported for Jet A with 15-percent aromatics.<sup>(14)</sup> Instead of increasing the aromatic content, the use of a carrier fluid\*\* was found to reduce the orifice flow to an acceptable level.

The data in Table 1 summarize the effect of base fuel properties and polar additives on the mist-ignition resistance of AMK. This mist-

\* British Standard 1733.

\*\* The carrier fluid is a proprietary material that was developed by ICI Ltd.

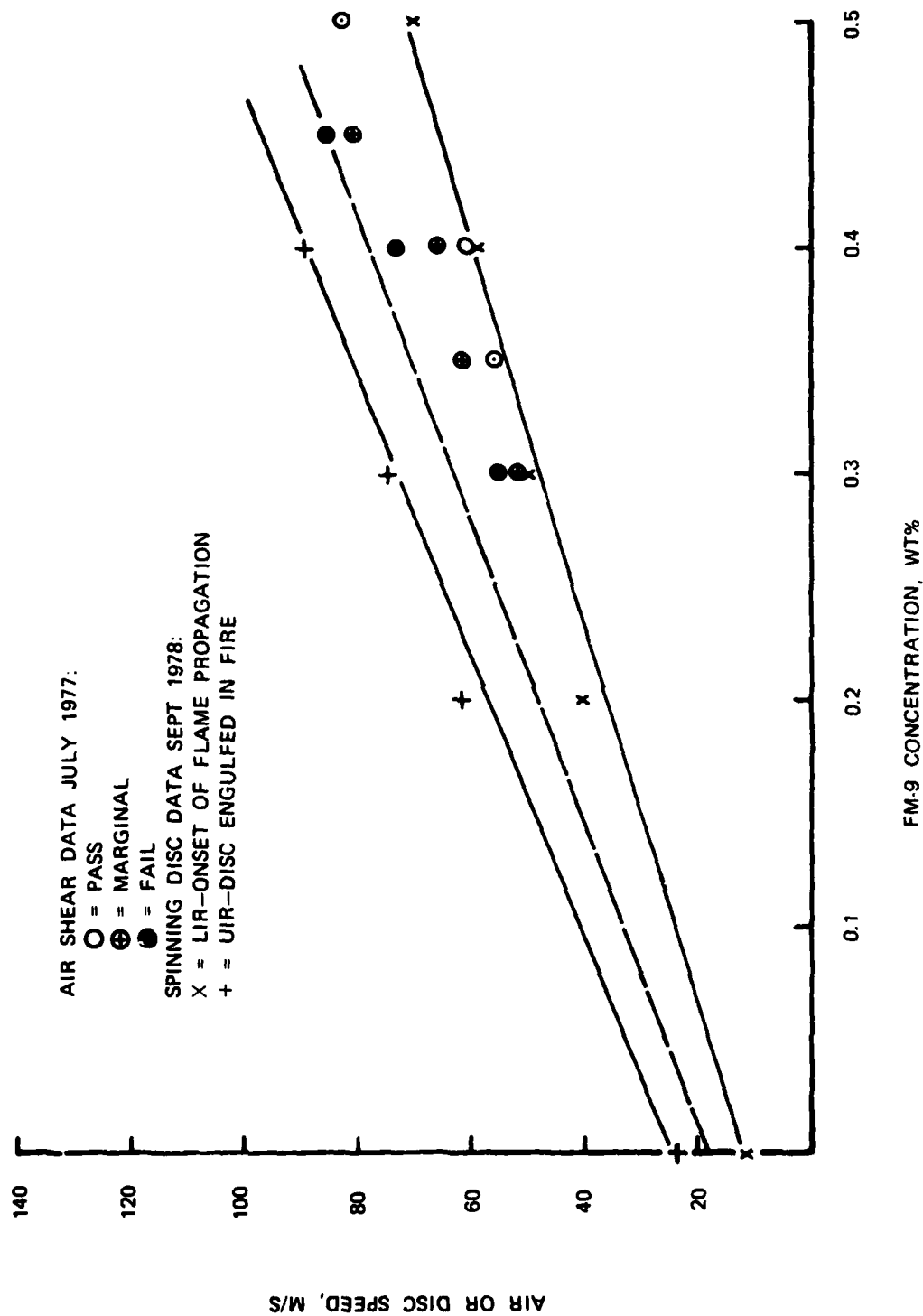


FIGURE 11. COMPARISON OF MIST IGNITION RESISTANCE OF FM-9 IN JET A WITH FUEL SPILLAGE/AIR SHEAR DATA

TABLE 1. EFFECT OF BASE FUEL AND SURFACTANTS ON  
THE MIST IGNITION RESISTANCE OF AMK (0.3% FM-9)

Base Fuel Consumption	Approx. Age, Weeks	Mist Ignition Resistance	
		LIR, m/s	UIR, m/s
Jet A (1.5 cP at 25°C)			
8% Aromatics	1	38-41	56-58
8% Aromatics	1	43-46	64-66
18-20% Aromatics	1	48-51	72-75
18-20% Aromatics	1	51-53	79-83
18-20% Aromatics	1	51-53	69-71
18-20% Aromatics	1	54-57	69-73
18-20% Aromatics	1	50-53	73-76
Jet A + Carrier	2-4	68-71	84-87
Jet A + Carrier	16-18	72-74	89-93
Jet A (18-20% Aromatics) + 0.5% SO-A	1	73-83	99-109
Jet A (18-20% Aromatics) + 0.5% SO-A**	1	89-98	99-110
Jet A (18-20% Aromatics) + 1.0% SO-A**	1	86-89	115
Jet A + Carrier + 0.5% SO-A	2-4	83-86	112-116
Jet A + Carrier + 0.5% + SO-A	16-18	79-80	106-109
Avtur (1.0 cP at 25°C)	16-18	57-60	73-76
15.5°C	16-18	50-54	66-69
32.2°C	16-18	47-50	67-69
Avtur + 0.5% SO-A	16-18	68-78	95-99
Avtur + 0.5% Span-80	16-18	67-69	88-93

\* Sample was received from Lockheed Georgia Company, Marietta, GA.

\*\* FM-9 powder was mixed with SO-A and was stirred into fuel without heat.

ignition resistance of 0.3% FM-9 in Jet A was increased approximately 10 m/s by increasing the aromatic content from 8 to 20 percent. The use of a carrier fluid (which does not prevent gel formation) increased the ignition resistance another 20 m/s. These results indicate that the fire safety of AMK can be affected by differences in the solubility characteristics of FM-9 in the base fuel.

In view of the observed effect of surfactants on preventing gel formation, the most surprising result of these experiments is the observed increase in ignition resistance of 0.3% FM-9 in Jet A upon the addition of 0.5-percent SO-A. The magnitude of this effect is quite significant for AMK made with U.S. (30 m/s) and U.K. (20 m/s) jet fuels; however SO-A has less effect (10 to 15 m/s) when the AMK contained carrier fluid. These results indicate that gel formation has little or no direct effect on antimisting effectiveness; therefore, it appears possible to use surfactants or other polar additives to improve both fire safety and fuel handling characteristics of FM-9 in Jet A. While the optimum surfactant content has not been determined, no significant increase in mist ignition was observed by increasing the surfactant from 0.5 to 1.0 percent. Based on preliminary screening tests, there is evidence that other surfactants may be effective at lower concentrations (0.1%)\*; however, only Span 80\*\* was tested in regard to ignition resistance and found to be comparable to SO-A.

Because of the potential importance of these findings, tests were performed in which a half-gallon jar of fuel was dropped from a height of 20 feet (impact velocity ~ 10 m/s) onto a steel plate surrounded by open flame ignition sources. The results showed a successively smaller fireball with (a) Jet A, (b) Jet A + 0.05% FM-9, and (c) Jet A + 0.05% FM-9 + 0.1% SO-A (Figure 12). Because of the relatively low atomization forces in this test, it was necessary to reduce the polymer and surfactant concentrations in order to see this effect. Nevertheless, these results add support to the mist-ignition measurements.

Currently, FM-9 powder is dissolved in Jet A by dispersing it into the fuel at room temperature and then heating it from 90° to 100°C at a

\* LT-10-8-1, Clintwood Chemical Co.

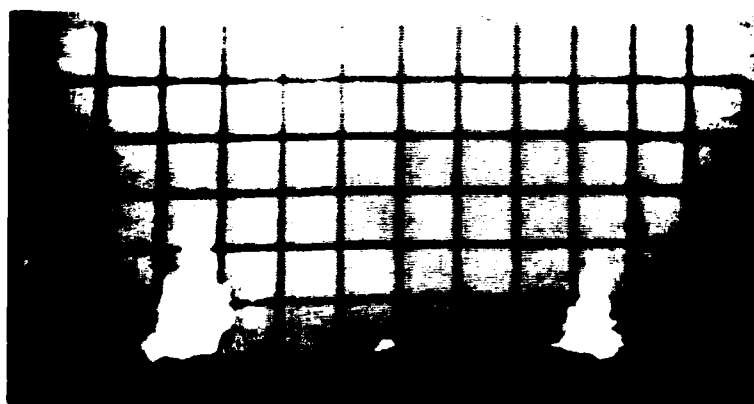
\*\* ICI Americas Inc., Atlas Chemical Div.



(A) JET-A



(B) JET-A + 0.05% FM-9



(C) JET-A + 0.05% FM-9 + 0.10% SO-A

FIGURE 12. EFFECT OF FM-9 AND FM-9/SO-A ON MAXIMUM FIRE-BALL SIZE OF JET A IN DROP TEST



mixing speed of close to 100 rpm. An interesting sidelight of the surfactant experiments is the finding that the surfactant can be used to solubilize the FM-9 powder without heating. The resulting AMK appears to be as effective (Table 1) as one in which the surfactant is added after the polymer has been solvated by heating. This result does not mean that the surfactant could take the place of the carrier-fluid that is now under development by RAE and ICI; however, it does suggest that an improved carrier may be formulated that results in rapid dissolution of the polymer but which also prevents gel formation that penalizes flow properties.

#### V. SUMMARY

Under certain conditions, antimisting kerosine consisting of Jet A and FM-9 polymer forms a flow-induced gel that plugs filters and capillaries. The filtration resistance of AMK can be greatly reduced either by heating the fuel to approximately 140°C or by the addition of a fuel-soluble surfactant. Both of these approaches are effective because of their abilities to reduce gel formation. Mechanical degradation of AMK produced by flow in packed tubes appears to be a promising method of restoring essential fuel properties; however, further development at higher energy levels will be required to completely restore both filtration and ignition properties.

Fire-safety effectiveness of AMK has been measured by a small-scale test. The mist-ignition resistance is reported in terms of the minimum fuel/air velocity that will support flame propagation. Results for different concentrations of FM-9 in Jet A appear to be in good agreement with the Fuel Spillage-Wind Shear Test. The ignition resistance of FM-9 in Jet A has been found to depend on fuel properties such as aromatic content and the presence of small amounts of polar additives. In particular, fuel-soluble surfactants that prevent gel formation have been found to increase ignition resistance by as much as 30-40 m/s. While the mechanism for increased fire safety has not been established, it is believed to be associated with improved solubility of FM-9 in Jet A. More importantly, these results indicate that gel formation is not

necessary for fire safety; consequently, it appears possible to utilize surfactants or similar additives to increase fire-safety effectiveness of FM-9 and also to reduce adverse fuel-handling properties associated with gel formation.

## VI. RECOMMENDATIONS

As a result of this program, the following recommendations are made:

1. Because of the controversial results in which surfactants were found to eliminate gelling and to increase the ignition resistance of AMK (0.3% FM-9 in Jet A), large-scale fire-safety experiments, such as the Rocket Sled and Fuel Spillage/Air Shear tests, should be conducted to determine the effect of surfactants on fire safety. Additional large-scale tests should be conducted to determine the predicted effects of fuel properties, such as aromaticity, carrier fluid composition, and polymer degradation.
2. The development of rheological tests that relate to flow properties such as filtration and apparent viscosity should be continued.
3. Polymer degradation by flow in porous media appears promising and additional experiments at higher pressures and with different porous media are needed.
4. Filtration experiments should be directed toward establishing the effect of filter properties on the flow resistance of partially degraded AMK.
5. Various types of hydrogen bonding agents should be investigated to determine their relative effectiveness in improving the fuel-handling and fire-safety properties of AMK.

## VII. LIST OF REFERENCES

1. Mannheimer, R.J., "Rheology Study of Antimist Fuels," FAA-RD-77-10, 1977.
2. Quadrat, O., and Bohdanecky, M., "Rheological Anomalies of Poly (Methyl Methacrylate) Solutions in Theta Solvents," *Polymer Letters*, 4, 833-835, 1966.
3. Quadrat, O., et al., "Influence of Thermodynamic Quality of a Solvent Upon Non-Newtonian Viscosity of Poly (Methyl Methacrylate) Solutions," *J. Polymer Sci.*, Part C, No. 16, 95-102, 1967.
4. Quadrat, O., and Bohdanecky, M., "Negative Thixotropy of Poly (Methyl Methacrylate) Solutions in Theta Solvents," *J. Polymer Sci.*, Part A-2, 5, 1309-1312, 1967.
5. Quadrat, O., "Investigation of the Conditions of Negative Thixotropy of Poly (Methyl Methacrylate) Solutions in Low Viscosity Solvents," *Collection Czechoslov. Chem. Commun.*, 36, 2042-2048, 1971.
6. Ibid, 37, 980-987, 1971.
7. Panov, Yu. N., et al, "Antithixotropy of Dilute Solutions of Copolymers of Methyl Methacrylate and Methacrylic Acid," *European Polymer Journal*, Vol. 4, 661-667, 1968.
8. Rouse, P.E., *J. Chem. Phys.*, 21, 1262-1279, 1953.
9. Marshall, R.J. and Metzner, A.B., "Flow of Viscoelastic Fluids Through Porous Media," *Ind. Eng. Chem. Fund.*, 5-7, 393, 1967.
10. Mannheimer, R.J., "Uncoiling of Flexible Macromolecules in Elongation Flow," U.S. Army MERADCOM ILIR Annual Report, 1977.

11. Ibid., 1978.
12. Miller, R.E. and Wilford, S.P., Unpublished report, RAE, Materials Dept., October 16, 1978.
13. San Miguel, A. and Williams, M.D., "Antimisting Fuel Spillage/Air Shear Tests at Naval Weapons Center," Technical Report FAA-RD-78-50, 1978.
14. Brooks, B., Unpublished report presented at Joint FAA-RAE-ICI Technical Meeting, Washington, D.C., November 27, 1978.